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BENÉT INTERNAL TECHNICAL REPORT

BITR NO. 91-6

AUTOMATIC COULOMETRIC TITRATION OF SULFURIC ACID IN CHROMIUM PLATING SOLUTIONS

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JUNE 1991



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Automatic Coulometric Titration of Sulfuric Acid In Chromium Plating Solutions

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Abstract

No specific chemical analysis method exists in the literature for the offline or online determination of sulfuric acid in chromium plating solutions by automatic coulometric titration. A method is presented here that provides somewhat acceptable analysis and monitoring of the sulfuric acid in this chromium plating process. Due to a subjective data reduction process, online application of this method is unacceptable. The optimum operating range of sulfuric acid is 2.40 - 3.10 g/l and the resulting precisions by this method are in the range of 0.10 - 0.25 g/l. These resulting offline automatic titration precisions are nearly equal to the presently used automatic ion chromatography precisions which is still the best available method to date.

Keywords

chemical analysis, sulfuric acid, chromium plating solutions, automatic coulometric titration

Acknowledgments

Sincere thanks are given to Jay Hoessle and Allison Montgomery of Benét Laboratories for their analytical chemistry work.

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Introduction

No specific chemical analysis method exists in the literature for the offline or online determination of sulfuric acid in chromium plating solutions by automatic coulometric titration.

A general chemical analysis method for the determination of sulfuric acid in the presence of chromic acid uses a method composed of a chromic acid reduction step followed by a barium chloride precipitation step to isolate barium sulfate for gravimetric measurement (ref 1). This method fails to adequately monitor the sulfuric acid in chromium plating solutions due to very poor precisions. Incidentally, these unacceptable precisions require three days of analysis time.

An instrumental chemical analysis method for the determination of sulfuric acid in chromium plating solutions uses an improved ion chromatographic method with conductimetric measurement and an extensive statistical evaluation of the experimental data (ref 2-4). This method makes the best offline attempt, to date, of chemically analyzing low concentration levels of sulfuric acid precisely, in the presence of high concentration levels of chromic acid, as required in chromium plating solutions. While analysis requires only a day, this method has been determined to require an unreasonable amount of maintenance for routine online monitoring.

Automatic coulometric titration is examined here to determine if it is an acceptable chemical analysis method for the given application in regard to precision, offline operation, and online operation.

Theory and Background

The analysis of liquids and solids by either manual or automatic titrimetry is one of the most important and useful methods in analytical chemistry. An explanation of this method is necessary for its evaluation as a chemical analysis technique.

Titration methods of analysis are based on measuring the total capacity of an analyte for a reagent. The three general types of titrimetry are volumetric titrimetry, gravimetric (weight) titrimetry, and coulometric titrimetry. In the first and second types, the volume or weight of a reagent of known concentration is required to react completely with the analyte determined. In the coulometric type, the "reagent" is a constant direct electrical current of known magnitude that reacts directly or indirectly with the analyte where the quantity measured is the time required for quantitative oxidation or reduction of the analyte (ref 5-6).

The basic types of titrations and measuring systems include precipitation-formation, acid-base, complex-formation, oxidation-reduction, photometric, conductometric, coulometric, polarographic, amperometric, and potentiometric methods (ref 5-10).

Titration is a quick, accurate, and widely used method for measuring the amount of substance in solution. A standard solution called a titrant is carefully measured by a buret and reacted with an unknown quantity of a second substance. If the volume and concentration of the titrant are known, the unknown quantity of the substance can be calculated. A titration is based on a chemical reaction that may be represented as:



where A is the titrant, B is the substance titrated, and a and b are the number of moles of each.

The main requirements of a titration are: 1) the reaction must be stoichiometric where a and b are whole numbers; 2) the rate of chemical reaction must be rapid; 3) the reaction must be 99.9% complete and quantitative when a stoichiometric amount of titrant is added; and 4) a method must be available for determining the point in the titration at which a stoichiometric amount of titrant has been added and the reaction is complete. Experimental detection of this point by an indicator color change or some change in an electrochemical or physical property of the solution is called the endpoint of the titration. The point at which the theoretical amount of titrant has been added is called the equivalence point of the titration. These two points should coincide but for various reasons may not (ref 5-6).

Approach

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 5). The experimental approach includes calibration and standardization with standard reference chromium plating solutions followed by analysis with sample chromium plating solutions. Calibration and standardization data are used to determine analyte concentrations of sample solutions.

The analytical system used is the Sanda Model FACTS automatic coulometric titrimeter in an experiment conducted at Sanda Corporation. This company publishes a manual which is an excellent source of reference for operation and maintenance of this instrument (ref 11). The specifications for this automated titration system include the thermometric application module, 0° to 100° C temperature range, sensitivity to 0.001° C, stability to 0.0002 % per °C, dispenser, thermistor sensor, 50 ml insulated titration vessel, automatic sample changer, printer, and computer. Polypropylene and teflon are used throughout the instrument where it comes in contact with these acidic sample solutions. The present price of the system is about \$15,000.

The analytical reagent grade standard solution required is a 2.95 ± 0.01 g/l sulfuric acid and 250 ± 1 g/l chromic acid binary solution that meets American Chemical Society (ACS), American Society For Testing Materials (ASTM) and Federal Standards (ref 12-15). EM Science reagent grade chromium trioxide is the only material found in our experience that meets ACS standards allowing a maximum of 0.005% sulfate. The other reagent grade solution required is the coulometric titrant, 1 M barium chloride. The analytical reagent grade standard solution above is used to standardize the barium chloride titrant solution.

Past work by this author (ref 4,16-18) provides extensive information for preparing, sampling, and chemically analyzing these standard and sample solutions for all analytes. These analytical chemistry methods are used for quality control purposes and are the best methods available to date. For the Benét offline ion chromatography sulfuric acid method, 1 ml of equivalent standard or sample chromic acid solution is used per replicate.

Preparation of a standard or sample solution for coulometric titration analysis requires that 25 ml of the undiluted solution is added to the titration vessel per replicate. Acetone may be added to sharpen the endpoint. Titrate using the coulometric titrant, thermistor sensor, and stirrer to a first and second derivative endpoint. The endpoint volume of the standard solution is "Reading 1" and of the sample solution is "Reading 2".

All standard and sample solutions are analyzed in triplicate. Sulfuric acid concentrations in the samples are calculated by normal chemical stoichiometry.

Results and Discussion

Experimental data is presented in Table 1 for the determination of sulfuric acid in the standard chromium plating solution. There is no trivalent chromium or iron in the standard solution. Experimental data is presented in Table 2 for the determination of sulfuric acid in the sample chromium plating solutions one and two. The respective chromic acid concentrations of sample solutions one and two are 244 and 255 g/l (ref 16). The respective trivalent chromium concentrations of sample solutions one and two are 1.8 and 4.1 g/l (ref 18). The respective iron concentrations of sample solutions one and two are 0.9 and 2.6 g/l (ref 17).

The explanation for the presence of barium sulfate precipitation and the lack of barium chromate precipitation is due to the fact that, in practical terms, all hexavalent chromium is in the dichromate form due to the undiluted standard and sample solutions with their pH's less than 0.5 pH units. Since the solubility products of each precipitate are in the same order of magnitude, the very slight presence of chromate does not interfere with sulfate despite a chromate-sulfate concentration ratio of one hundred (19).

Simple proportion is used to calculate the concentration of sulfuric acid in these sample solutions:

$$\text{g/l H}_2\text{SO}_4 = (2.9) \frac{\text{Reading 2}}{\text{Reading 1}} \quad (2)$$

where Reading 2 is the ml of sample titrant and Reading 1 is the ml of standard titrant.

Previously, the variations in precision were evaluated for the materials and methods used (ref 20).

One major problem associated with this technique is related to the data reduction of the heat curve. When first and second derivatives are taken of this heat curve data, the resulting spectra have considerable noise. A Fast Fourier Transform (FFT) smoothing technique is applied to reduce the noise but still the choice of the endpoint is subjective and requires considerable analyst interpretation. Acetone does not effect the dichromate-chromate ratio and is used for dilution to slow heat transfer and sharpen endpoints but no appreciable benefit is derived from this added step. An additional problem is related to the dispensing tip. Sanda does not use an anti-diffusion dispensing tip like many other titration system manufacturers. For fast titration reactions this results in sample reactants working their way up the dispensing tip. This can be minimized by raising the dispensing tip to a sufficient level above the reaction vessel solution but dispensing from this height further increases heat curve noise.

This method provides somewhat acceptable offline analysis and monitoring of the sulfuric acid in the chromium plating process. The optimum operating range of sulfuric acid is 2.40 - 3.10 g/l. The resulting precisions by this method are in the range of 0.10 - 0.25 g/l and are nearly equal to the presently used automatic ion chromatography precisions which is still the best available method to date. Due to the subjective data reduction process, the technique of automated coulometric titration is not recommended for online chemical analysis for the given application.

Table 1. Determination Of Sulfuric Acid In The Standard Chromium Plating Solution

Replicate	Benet Conc. (g/l)	Sanda Conc. (g/l)
1	2.8	2.6
2	3.0	3.0
3	2.8	2.7
Mean	2.9	2.8
Std Dev	< 0.1	0.2

Table 2 - Determination Of Sulfuric Acid In The Sample Chromium Plating Solutions

Replicate	Sample One		Sample Two	
	Benet Conc. (g/l)	Sanda Conc. (g/l)	Benet Conc. (g/l)	Sanda Conc. (g/l)
1	2.7	2.8	2.9	2.7
2	2.7	2.6	2.8	2.5
3	2.5	2.5	2.9	3.0
Mean	2.6	2.6	2.9	2.7
Std Dev	< 0.1	0.1	< 0.1	0.2

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